Discussion of “Kinetics of Iron Corrosion in Concentrated Acidic Chloride Solutions” [E. McCafferty and Norman Hackerman (pp. 999–1009, Vol. 119, No. 8)]

Bech-Nielsen, Gregers

Published in:
Journal of The Electrochemical Society

Link to article, DOI:
10.1149/1.2403558

Publication date:
1973

Document Version
Publisher's PDF, also known as Version of record

DISCUSSION SECTION

This Discussion Section includes discussion of papers appearing in the *Journal of The Electrochemical Society*, Vol. 119, No. 5, 8, and 10; May, August, and October, 1972.

Anodic Oxidation of Ethylenediaminetetraacetic Acid on Pt in Acid Sulfate Solutions

J. W. Johnson, H. W. Jiang, S. B. Hanna, and W. J. James

(pp. 574-580. Vol. 119, No. 5)

P. Sidheswaran, V. K. Venkatesan, and H. V. K. Udupa:[1] During the steady-state oxidation of EDTA at platinum electrodes in acid sulfate solutions, Johnson *et. al.*, in the paper under discussion, identified various reaction products. A definite clue to the presence of CH_2O was obtained from the melting point of the DNP derivative. However, it is very easy to establish the presence of CH_2O with chromotropic acid by the method described elsewhere.[2] After 3 hr of electrolysis, we also noticed[3] a concentration of $>10^{-2}$M CH_2O formed from 0.5M EDTA. Our evidence strongly supports their observation that CH_2O is thrown out into the solution.

The formation of CH_2O has been indicated to be due to a reverse Schiff-type reaction and the authors of the above-mentioned paper proposed the following two steps

$$R{-}\overset{\overset{Ac}{|}}{N}{-}CH_2\cdot + H_2O \rightarrow R{-}\overset{\overset{Ac}{|}}{N}{-}CH_2OH + H\cdot \qquad [19]$$

$$R{-}\overset{\overset{Ac}{|}}{N}{-}CH_2OH \rightarrow R{-}\overset{\overset{Ac}{|}}{N}{-}H + CH_2O \qquad [20]$$

However, the second step should be either less probable or a simultaneous reaction occurs on the platinum electrode. This opinion stems from the following evidence: Podlovchenko *et al.*[4] have demonstrated that the presence of a hydroxyl function weakens the C-C bond; it has also been noticed by us[3] that primary alcohols preferentially get disintegrated into two fragments of which CH_2OH is one. The mechanism of formation of CH_2O from CH_2OH has already been proposed.[2] Hence, the following mechanism appears to be operative

$$2Pt + R{-}\overset{\overset{Ac}{|}}{N}{-}CH_2OH \rightarrow R{-}\overset{\overset{Ac}{|}}{\underset{\underset{Pt}{|}}{N}} + \underset{\underset{Pt}{|}}{CH_2}OH \qquad [1]$$

$$H{-}\overset{\overset{H}{|}}{C}{-}O{-}H \rightarrow H{-}\overset{\overset{H}{|}}{C}{=}O + Pt + Pt \qquad [2]$$

The observed Tafel slope of ~120 mV is in sharp agreement with $\beta \approx 0.5$ and $\Delta Ea/\Delta\psi r \approx 14$ kcal/mole/V. However, it is very difficult to establish exactly which step decides the rate of the entire reaction in as much as so many reaction intermediates are getting formed and oxidized.

J. W. Johnson, H. W. Jiang, S. B. Hanna, and W. J. James: We were very interested to learn of the similar work with EDTA that has been done by Sidheswaran, Venkatesan, and Udupa, and of the close agreement of the experimental results of the two studies. Our difference in interpreting the results appears to center around the disposition of the species, $R{-}\overset{\overset{Ac}{|}}{N}{-}CH_2OH$, which was proposed as an intermediate. In particular we have proposed a homogeneous, nonelectrochemical step (reverse Schiff-type) by which formaldehyde is ejected from the intermediate. Venkatesan *et al.* propose a heterogeneous step that results in two adsorbed fragments, one of which (CH_2OH) is the precursor of formaldehyde.

A sequence such as proposed by Venkatesan *et al.* was among the many that we considered. The one presented in our paper was favored because of the following reasons.

If bonding should occur between Pt and the nitrogen atom as shown in Step I (SVU sequence), several desorption and readsorption steps would be necessary to account for all the observed reaction products, *e.g.*, ED3A, U-EDDA, S-EDDA, and EDMA. This does not seem likely. A further consideration is the geometrical crowding around the nitrogen atom by other attached groups that makes its accessibility unfavorable for bonding with the electrode. Finally, protonation of the unshared electron pair on the nitrogen atom is also quite likely which would further hinder its adsorption.

If formaldehyde were produced as shown in Step II of the SVU sequence, the further ionization of the adsorbed H would be almost certain, and be associated with a 1 CO_2/2**F** coulombic relationship. This relationship was not observed experimentally, though the observed value could be accounted for by a combination of the SVN and JJHJ sequences.

Our studies indicate that EDTA is oxidized on Pt at potentials up to *ca.* 1.6V. It is doubtful that oxide-free sites would be available for bonding at these potentials[5] as required by the SVN sequence. Since no change in the reaction sequence with potential is indicated by the experimental results, we feel that direct bonding (adsorption) between Pt atoms and the EDTA species or any fragments therefrom should be excluded.

In summary, the sequence proposed by Venkatesan *et al.* is a logical one and cannot be completely eliminated as a possibility. Indeed it may be that both sequences (or others) are occurring. However, the above mentioned items caused us to favor the sequence we proposed.

Kinetics of Iron Corrosion in Concentrated Acidic Chloride Solutions

E. McCafferty and Norman Hackerman (pp. 999-1009, Vol. 119, No. 8)

G. Bech-Nielsen:[6] This paper, and also a virtually simultaneous publication by Darwish, Hilbert, Lorenz, and Rosswag,[7] report some important and rather unusual kinetic data for iron electrodes in strongly acid, strongly concentrated, chloride solutions. In the two papers reaction schemes of a similar type are proposed for explaining the observed kinetic parameters.

We would like to point out that such unusual kinetic parameters have been reported previously, to-

[1] Fundamental Electrochemistry Section, Central Electrochemical Research Institute, Karaikudi 3, Tamil Nadu, India.
[2] P. Sidheswaran, *J. Electroanal. Chem.*, 38, 101 (1972).
[3] P. Sidheswaran, Unpublished work.
[4] B. I. Podlovchenko and V. F. Stenin, *Elektrokhimiya*, 3, 649 (1967).
[5] S. Gilman and M. W. Breiter, *This Journal*, 109, 1099 (1962).
[6] Chemistry Department A, The Technical University of Denmark, Lyngby, Denmark.
[7] N. A. Darwish, F. Hilbert, W. J. Lorenz, and H. Rosswag, 23rd Meeting of ISE, Extended Abstracts p. 213, Stockholm, 1972.

gether with the more usual ones, for iron electrodes in a wide variety of solutions.[8-11] It may well be that all of the unusual parameters will be found simultaneously only when using extremely concentrated solutions, whereas it has been shown that dilute, less concentrated, solutions present conditions for observing first (at lower anodic potentials) the usual behavior called the I_1-reaction[8-11] and then, following a characteristic transition region, the less usual or less often examined behavior of the I_2-reaction.

The most constant feature of this latter reaction is the higher Tafel slope (from *ca.* 80 to more than 120 mV), while the reaction orders with respect to different anions may be negative[10] or positive,[9] and the reaction order with respect to *p*H has been reported to be positive[10] or zero.[11] (A further indication of transition from negative to positive values has been found, but not yet published, in data from the experiments with an NH_4ClO_4-$NaClO_4$ solution, *p*H 5.5-3.0 described elsewhere.[9])

It is not surprising that neither the discussed paper nor that of Darwish *et al.* include descriptions of simultaneous observation of the two distinct reactions, since it can be seen,[11] and may be shown by general considerations,[12] that the regions, where a distinct behavior in accord with either of the reactions will be found, are likely to be separated by some 1-3 decades of current density (C.D.). When the I_2-reaction is recorded in the range of moderate anodic C.D.'s, it may be inferred that the I_1-reaction is only found in the C.D. range below the corrosion C.D., which is in accord with the usual inhibitive influence on this reaction of low *p*H and high chloride concentration together with the promotion of the hydrogen evolution reaction caused by lower *p*H.

Since we have observed that the I_1 and the I_2 reaction usually occur together as coupled, parallel reactions, we have suggested an outline of a kinetic model, which accounts for the potential-dependent transition between the two processes.[9] An explanation of this feature is evidently of primary importance, and further examination of the influences of *p*H and anions in the individual steps of the two reactions are now in progress.

In the last part of this comment we should like to consider the so-called reaction orders with respect to *p*H ($-\partial \log i/\partial \log [H^+]$). The analysis of coupled, parallel reactions developed by us indicates that the I_2 reaction proceeds via an intermediate complex of the composition $Fe^{II}(OH^-)_3(X)$, where X is a ligand, usually an anion.[8,9] In most cases known to us (of which one has been reported),[10] the reaction order with respect to *p*H for the I_2 reaction is between 0.2 and 0.3, *i.e.*, much lower than the number of OH^- ions taken up during formation of the intermediate complex. We therefore suggest that the observation of a negative reaction order with respect to *p*H for the I_2 reaction does not necessarily require the assumption of uptake of H^+ ions (especially not when the observation is possible at intermediate *p*H values, as we have seen). The steps in the mechanism following the formation of the above-mentioned complex should merely involve removal of one or more of the OH^- ions (in exchange for halide ions, for example) by H^+ ions, in order to result in an over-all negative reaction order with respect to *p*H (and at the same time a positive one for the halide ion).

E. McCafferty and Norman Hackerman: We thank G. Bech-Nielsen for his interesting comments and for calling our attention to the work of Darwish, Hilbert, Lorenz, and Rosswag.[7] These workers have confirmed our observation that both H^+ and Cl^- ions promote iron corrosion in concentrated acidic chloride solutions (*i.e.*, the reaction orders z_{H+} and z_{Cl-} are positive), in contrast to the usual cases more frequently examined (more dilute solutions) for which both z_{H+} and z_{Cl-} are negative.

Table I. Polarization resistance for iron in 6*N* chloride solutions.

N [H+]	Polarization resistance (ohm-cm²) Polarization curve	Calc'd from Stern-Geary Eq.
1.2	38.6	40.1
2.4	20.4	24.1
3.6	21.4	18.8
4.8	10.3	15.7
6.0	6.3	9.5

Both our results in the paper under discussion and the Darwish data[7] have shown that a high concentration of hydrogen ions in combination with a high concentration of chloride ions is necessary to give the new set of parameters $z_{H+} = +1$[7] as compared to +1.8 in our paper; $z_{Cl-} = +0.5$ in both our results; and $b_a =$ 60-80 mV in our paper as compared to 120 mV in the work of Darwish *et al.*

These parameters are unusual in the sense that the signs of z_{H+} and z_{Cl-} in certain concentrated solutions are opposite to those in differing, dilute solutions. In contrast, in the work of Bech-Nielsen, the unusual parameters emerged only after considerable anodic polarization (usually about 200 mV) in the same solution. The possibility that the original surface could have been modified seems to have been recognized by the authors, who usually attributed the second Tafel region to the appearance of passivation precursors.

Whether or not the two sets of observations are linked through a general scheme of coupled, parallel, reactions having widespread validity remains to be seen. We did not examine the region below the corrosion current density in any great detail, but our own data do tend to show simple pre-Tafel behavior rather than the existence of a different, *i.e.*, I_1, reaction. Table I compares polarization resistances obtained from the linear polarization curve near the corrosion potential (Fig. 1) with those calculated from the Stern-Geary equation.[13] Agreement between the two sets of values is generally good, although a more thorough examination of the region close to the corrosion potential should be made, as suggested by Bech-Nielsen.

We next consider the suggestion that replacement of adsorbed OH^- ions by Cl^- (to give positive z_{H+} and z_{Cl-}) is equivalent to uptake of H^+ ions by adsorbed Cl^-. Consider the two reaction mechanisms in Table II. Mechanism I involves adsorption of Cl^- ions by replacement of chemisorbed water molecules,[14] followed by attraction of H^+ ions onto chemisorbed $FeCl^-_{ads}$, as

[8] H. Nord and G. Bech-Nielsen, *Electrochim. Acta*, **16**, 849 (1971).
[9] G. Bech-Nielsen and J. C. Reeve, 6th Scandinavian Corrosion Congress, chap. 8, Gothenburg, 1971.
[10] G. Bech-Nielsen, 23rd Meeting of ISE, Extended Abstracts, p. 213, Stockholm, 1972.
[11] I. Epelboin and M. Keddam, *Electrochim. Acta*, **17**, 177 (1972).
[12] G. Bech-Nielsen, Submitted to *Electrochim. Acta*.
[13] M. Stern and A. L. Geary, *This Journal*, **104**, 56 (1957).
[14] T. N. Andersen and J. O'M. Bockris, *Electrochim. Acta*, **9**, 347 (1964).

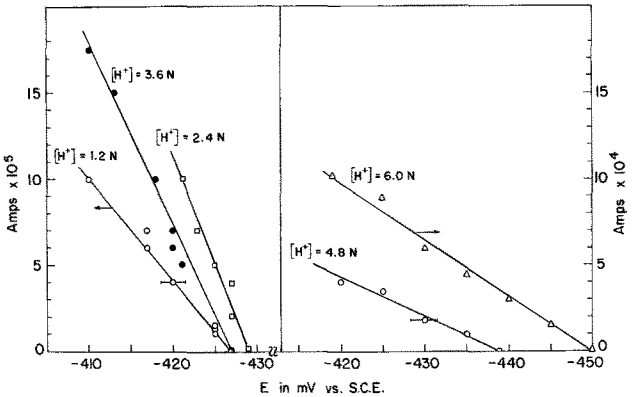

Fig. 1. Polarization curves near the corrosion potential for 6*N* chloride solutions of various acidities.